
Water Vapor Isotherms and Heat of Immersion of Na- and Ca-Montmorillonite Systems. III. Thermodynamics¹

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Abstract: The integral thermodynamic quantities of adsorbed water on Na- and Ca-montmorillonite have been calculated from water adsorption isotherms on Na- and Ca-montmorillonite at 298° and 313° K and from one adsorption isotherm and calorimetric measurements at 298° K. The integral entropy values decrease and then increase as the amount of adsorbed water approaches zero. In both systems, the curves approach the entropy value of free liquid water at the high content water. The thermodynamics of adsorbate on a non-inert adsorbent is discussed in some detail. The two-isotherm method gives the energy change of the water phase only, whereas the calorimetric method gives the energy change of the whole system (clay, exchangeable cations, and the adsorbed water). Only when the energy changes in the solid phase are negligible (=inert surface) should the two methods give similar results. An hypothesis was developed to explain the entropy-change data of water adsorbed on clay surfaces, in which the clay surface behaves as a non-inert adsorbent.

Key Words: Adsorption • Heat of immersion • Montmorillonite • Thermodynamics • Water

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